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Review article

Recent advances in surface active ionic liquids (SAILs): A Review

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ABSTRACT

Ionic liquids (ILs) have evolved from obscure compounds to significant components of modern chemistry, characterized by their ability to exist in the liquid phase at moderate temperatures without additional solvents. Surface-active ionic liquids (SAILs), exhibiting amphiphilic properties akin to traditional surfactants, hold promise for enhancing interfacial processes. Understanding the thermodynamic and surface parameters governing micelle formation in ILs provides crucial insights into their behavior and applications. Recent research has showcased the potential of SAILs in enhanced oil recovery (EOR) and medical treatments, offering solutions for improving oil recovery efficiency and exploring medical applications such as cancer treatment. This highlights the versatility and efficiency of SAILs across various fields of chemistry, paving the way for greener and more sustainable practices.

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1. Introduction

Ionic liquids (ILs) are typically defined as compounds entirely composed of ions with a melting point below 100 °C [1-3]. The first IL, ethylammonium nitrate, was discovered by Paul Walden in 1914. However, at that time, Walden did not anticipate that ILs would emerge as a significant scientific field nearly a century later. Indeed, ILs as innovative fluids have garnered considerable attention only in the past two decades. The number of scientific papers on ILs published in journals indexed by the Science Citation Index (SCI) has shown an exponential increase from just a few in 1996 to over 7000 in 2023. This growth rate has surpassed that of many other popular scientific areas. Such trends suggest a growing interest among researchers in exploring this fascinating field, leading to a wealth of outcomes [4, 5]. At its core, an ionic liquid is essentially a type of salt. If you imagine common table salt (NaCl), you're on the right track. Salts are compounds comprised of positively-charged cations and negatively-charged anions. Typically, these charges balance each other out, rendering the compound electrically neutral. For instance, NaCl consists of the $Na+$ cation and the $Cl–$ anion. What sets ionic liquids apart is their ability to exist in the liquid phase, distinguishing them from many traditional salts encountered in chemistry laboratories. Traditional salts like NaCl or KCl are solid at room temperature and only become liquids at extremely high temperatures, at around 800.7 °C for NaCl and 770 °C for KCl. In this molten state, they are referred to as "molten salts." To convert table salt into a liquid form at room temperature, you would typically dissolve it in water, resulting in an ion solution rather than an ionic liquid [6]. Ionic liquids (ILs), however, remain in a liquid state at more moderate temperatures without the need for dissolution in another solvent. The growing emphasis on safe, sustainable, and environmentally friendly chemistry, coupled with increasing regulatory pressure, has created a demand for greener chemical processes. One significant aspect of this endeavor is the reduction of organic solvent usage, which often accounts for over 50% of the materials employed in the production of drugs and other fine chemicals. Various factors influence solvent selection, including safety considerations such as flammability and stability, environmental toxicity, waste generation, and reaction efficiency [7, 8]. Among the innovative solutions are surface-active ionic liquids, a notable class within the broader category of ILs. These substances offer potential benefits for a range of applications, contributing to the development of greener and more sustainable chemical processes. Top of Form Ionic liquids featuring long alkyl chains represent a novel category of amphiphiles known as surface-active ionic liquids (SAILs). These compounds often exhibit amphiphilic characteristics similar to surfactants, owing to their distinct hydrophilic head and hydrophobic tail structures. This composition grants them the ability to self-organize into micelles and exhibit surface activity. The surface activity of SAILs is characterized by a low critical micellar concentration (CMC), enabling them to reduce interfacial tension (IFT) even under high salinity and temperature conditions. Understanding the thermodynamic and surface parameters of micelle formation provides valuable insights into the driving forces behind aggregation. Parameters such as the CMC and krafft temperature of ILs offer significant information about their surface-active properties, with ILs demonstrating reduced effectiveness below the krafft temperature. Moreover, ILs with higher krafft temperatures have been shown to more effectively reduce surface tension [9-12]. These observations underscore the importance of considering both thermodynamic and surface parameters when assessing the surface-active properties of ILs, particularly in applications where interfacial phenomena play a crucial role [13].

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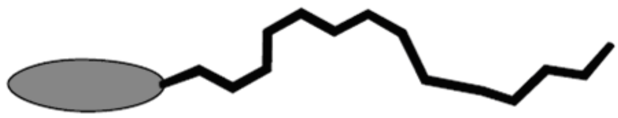
Table 1: Table showing typical characteristics of surfactants and their applications

Applications	**Characteristics**
Detergency	Low CMC, good salt and pH stability, biodegradability, desirable foaming properties
Emulsification	Environmental and biological (safety) for application
Lubrication	Chemical stability, adsorption at surfaces
Mineral flotation	Proper wetting of oil-bearing formations, microemulsion formation and solubilization properties, ease of emulsion breaking after oil recovery
Pharmaceuticals	Biocompatibility, low toxicity, proper emulsifying properties

2. Surfactants

Surfactants, short for surface-active agents, are incredibly versatile compounds utilized across various industries. Their primary function involves lowering surface tension at interfaces, rendering them indispensable in household cleaners, pharmaceuticals, and drilling fluids [14-19]. These molecules possess amphiphilic properties, featuring both hydrophobic and hydrophilic components that orient themselves at air-water interfaces.



Hydrophilic head group Hydrophobic tail

Figure 1 Structure of a surfactant monomer.

Surfactants can be characterized by the number of tails they possess, with some having a single tail and others featuring double chains. They are further classified based on the nature of their polar head groups, which can be anionic (carrying a negative charge), cationic (carrying a positive charge), zwitterionic (containing both positive and negative charges), or nonionic (lacking a net charge). Anionic surfactants, such as sulfates and sulfonates, are commonly employed in cleaning products due to their effectiveness. Cationic surfactants, exemplified by alkyl ammonium chlorides, carry a positive charge and find applications in various industries. Zwitterionic surfactants, represented by betaines, possess both positive and negative charges, contributing to their unique properties. Nonionic surfactants, like ethoxylates, do not carry a net charge and are less affected by water hardness. They excel at emulsifying oils and removing organic soils, making them suitable for a wide range of applications. Overall, surfactants play a crucial role in numerous industrial processes, owing to their ability to modify surface properties and facilitate various interfacial phenomena [20-21]

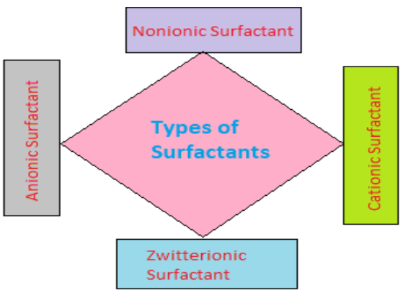


Figure 2: Picture showing different types of surfactants

3. Critical Micelle Concentration (CMC) of surfactant

Surfactant molecules have a natural affinity for accumulating at interfaces or surfaces between two phases. However, when the interface becomes saturated with surfactant molecules, they start to group in the liquid phase. These clusters of surfactants are known as micelles. In polar liquids, surfactant molecules arrange their non-polar chains so that their polar head groups extend into the liquid phase. Conversely, in non-polar liquids, inverse micelles form, where the headgroups cluster together while the non-polar hydrocarbon chains orient towards the surrounding phase. Micelles can adopt various shapes, with spherical micelles being one common form where surfactants arrange themselves in a spherical configuration. However, by varying parameters such as temperature and system composition, surfactants can also form elongated or worm-like structures. In addition to micelles, liquid crystals can also form layered structures of surfactant molecules. These complex arrangements arise from the interplay between molecular properties and external conditions, offering a rich landscape for exploring the behavior of surfactant systems. Determining the critical micelle concentration (CMC) is a fundamental chemical-physical parameter for characterizing pure surfactants in terms of their surface activity and self-assembled aggregation [22]. Various techniques such as tensiometry, conductivity, and fluorescence spectroscopy can be employed to calculate CMC values. These methods are capable of tracking the changes in physical properties corresponding to surfactant concentrations [23-25].

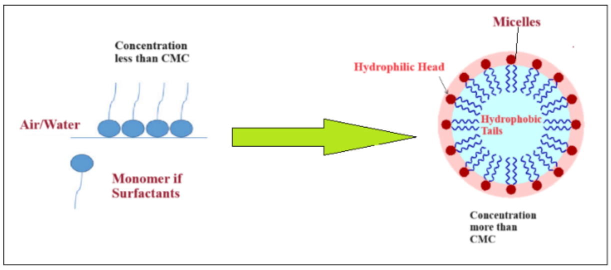


Figure 3: Schematic illustration different stages of surfactant with concentration.

4. Surface active ionic liquids (SAILs)

Katharina Bica-Schröder et al. [26], shed light on the unique properties and applications of SAILs in their review and illustrated how certain ionic liquids can function as surfactants in aqueous environments, allowing for the creation of solvent systems with distinctive characteristics. The chemistry of SAILs in water differs significantly from that of traditional molecular solvents, leading to a surge in their utilization across various fields of chemistry. The review delves into the structural features of SAILs and their ability to aggregate in water, forming micellar structures. Characterization techniques for these micelles are explored, along with discussions on aggregation and methods for studying micellization behavior. Furthermore, the review highlights the diverse applications of SAILs across different branches of chemistry, ranging from traditional organic chemistry to nanoparticle synthesis. Overall, Bica-Schröder et al.'s review provides valuable insights into the properties, behavior, and applications of SAILs, contributing to our understanding of these compounds and their potential impact on various areas of research and industry. Mandal and colleagues [27], conducted a study focusing on the synthesis and characterization of SAILs with potential applications for enhanced oil recovery (EOR). Their research involved a comprehensive laboratory estimation of the synthesized SAILs to evaluate their physicochemical properties and suitability for

EOR purposes. Using techniques such as FT-IR, ^{1}H NMR, and thermogravimetric analysis, they established the chemical properties and thermal steadiness of the synthesized SAILs, specifically C_{12}mimBr and C_{16}mimBr. Subsequently, the surface-active characters of these SAILs in aqueous solutions were explored to determine their behavior at reservoir conditions. Their findings revealed that the synthesized SAILs exhibited a lower CMC, approximately 200 ppm for C_{16}mimBr, indicating their effectiveness as surfactants. Moreover, these SAILs demonstrated high efficiency in reducing interfacial tension, achieving ultra-low values ranging from 0.001 to 0.0001 across a broad range of salinity, concentration, and temperature conditions. Furthermore, phase behavior evaluation suggested the creation of WINSOR-III micro-emulsions, highlighting the robust performance and potential applicability of these SAILs in EOR processes. Gupta and her colleagues [28], have given a comprehensive review of the application of SAILs in EOR processes giving insights into recent research progress in this area, highlighting key findings: (a) SAILs have amphiphilic character, act as surfactants, and have less CMC compared to conventional surfactants with similar structure, (b) Many conventional surfactants used in EOR processes do not function well at the inflated salinity conditions typically established in oil pools.To give an example, the Yibal gusher in Oman has an emergence salt concentration of 20%, while In North America, the Bakken formation encounters a challenging environment characterized by elevated salinity levels, typically ranging from 15% to 30% total dissolved solids (TDS), along with high temperatures spanning from 80-120 degree Celsius. Anionic surfactants that have a negative charge are spurned for flooding in carbonate lochs because they are more likely to be lost due to adsorption. Additionally, the presence of divalent ions in formations can cause anionic surfactants to precipitate out of solution. In these cases, cationic surfactants are a better choice for use in surfactant-containing EOR processes for CO_3^{2-} productions. Most Surfactant-Ammonium Ionic Liquids (SAILs) are cationic. Compared to conventional surfactants, SAILs are more effective at reducing the IFT between crude oil and water, making them a potential solution for used in EOR procedures for CO_3^{2-} formations. They can work freely even at low concentrations, which helps make amends for their higher cost. Furthermore, even under elevated temperatures and salt concentration conditions, SAILs are more effective than normal cationic and anionic surfactants, (c) SAILs that have a heterocyclic controller group display a towering IFT compared to those with aliphatic ones. Increased hydrophobicity of heterocyclic SAILs is the reason for their enhanced interfacial activity. Heterocyclic SAILs, particularly those with an aromatic headgroup, maintain their ability to reduce IFT even in high-salt environments. Aromatic headgroups interact strongly with crude oil components like aromatics, asphaltenes, and resins, leading to significantly decreased IFT values (to around 10^{-2} mN/m). In elevated salinity conditions, the lipophilic nature of the aromatic headgroup becomes pivotal for enhancing IFT reduction efficiency, (d) When few specific SAILs are introduced into an oil well, they may not be effective in decreasing IFT between the oil and H_2O to low enough levels for use in EOR operations. However, this issue can be addressed by adding certain specific cosolvents, known as cosurfactants, that work together with the SAIL to achieve the desired reduction in IFT. SAILs can also be combined with conventional surfactants or alkalis to achieve ultralow IFT values between crude oil and brine, as well as between acidic crude oil and injected slugs. The use of SAIL + alkali combinations can help to reduce the overall price of EOR exercise, (e) In recent times, bi-amphiphilic SAILs have been discovered to lower interfacial tension to very low values 0.001 mN/m without the requirement for any additional additives. Such SAILs have an asymmetric structure that creates equilibrium between the hydrophobic and hydrophilic parts, thus increasing their IFT by several folds and raising their capability to form more stable aggregation structures. The literature presents various examples of SAILs, such as proline ionic liquids (ProILs) featuring the alkyl chain connected to the anionic group, 72 imidazolium-based SAILs containing an anionic part with an elongated water-repellent tail, and 44 phosphonium-based SAILs characterized by a biamphiphilic configuration, (f) SAILs have potential to be used in EOR processes due to various advantages they offer. One such advantage is that SAILs escalate the viscosity of the introduced fluid, which leads to an improved mobility ratio. Additionally, SAILs have the ability to change the wettability of rocks from oil-wet to water-wet, which is another potential mechanism for EOR processes. Harsh Kumar and his research group [29] have studied the effects of amino acids on the surface fusion and aggregation properties of surface-active ionic liquids with varying +ve head groups. Amino acids are molecules that contain both amino and acidic groups within the same molecule [30-31]. They compared the micellization behavior of a morpholinium-based IL and an imidazolium-based IL with the same water-repellent alkyl chain length (n = 12) in the presence of an amino acid (AA) L-methionine. They used different methods including electrical conductivity, surface tension, UV-visible spectroscopy, and DLS measurements. The CMC data obtained through the 3 techniques are in complete agreement with each other and DLS measurements were used to determine the aggregates size, which showed that the size of micelles decreased with AA addition in both ILs. This supports the fact that water-repellent interactions dominate at larger concentrations of AA. The micellization character of both ILs was found to be improved with the addition of the AA- L-methionine. Therefore, there are higher chances of using such a mixture in medical uses, especially in cancer cure.

5. Future Outlook for Surface Active Ionic Liquids

Surface-active ionic liquids (SAILs) hold immense promise as versatile compounds with applications across various fields. Their future outlook appears bright, as ongoing research continues to unveil their potential in diverse areas such as catalysis, nanotechnology, and environmental remediation. With unique properties stemming from their dual nature as both ionic liquids and surfactants, SAILs offer opportunities for tailored design to meet specific application requirements. Moreover, their tunable surface activity and compatibility with aqueous and organic systems enhance their versatility. As advancements in synthesis methods and understanding of their behavior at interfaces progress, SAILs are poised to revolutionize industries ranging from pharmaceuticals to energy. Additionally, their environmentally friendly nature, marked by low volatility and recyclability, positions them as sustainable alternatives to traditional surfactants. In the coming years, continued exploration and innovation in SAIL research are likely to unlock new avenues for their utilization, paving the way for transformative technological advancements.

6. Conclusion

Ionic liquids (ILs) have come a long way from being relatively unknown compounds to becoming significant players in modern chemistry. ILs are a unique class of salts that can exist in the liquid phase at moderate temperatures without additional solvents. They offer exciting prospects for enhancing interfacial processes, particularly through surface-active ionic liquids (SAILs) that exhibit amphiphilic properties like traditional surfactants. Understanding the thermodynamic and surface parameters governing micelle formation in ILs provides invaluable insights into their behavior and potential applications. ILs, especially SAILs, are promising for a greener and more sustainable future in various fields of chemistry. Recent research has highlighted the potential applications of surface-active ionic liquids (SAILs) in enhanced oil recovery (EOR) and medical treatments. SAILs have shown promise as efficient surfactants for EOR processes, offering potential solutions for improving oil recovery efficiency while addressing challenges such as high salinity and temperature environments. SAILs also have potential medical applications, particularly in cancer treatment. The research presented underscores the potential of SAILs as versatile and efficient agents in various fields.

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